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Development of high temperature PEM fuel cells. Simplification and CO tolerance mapping

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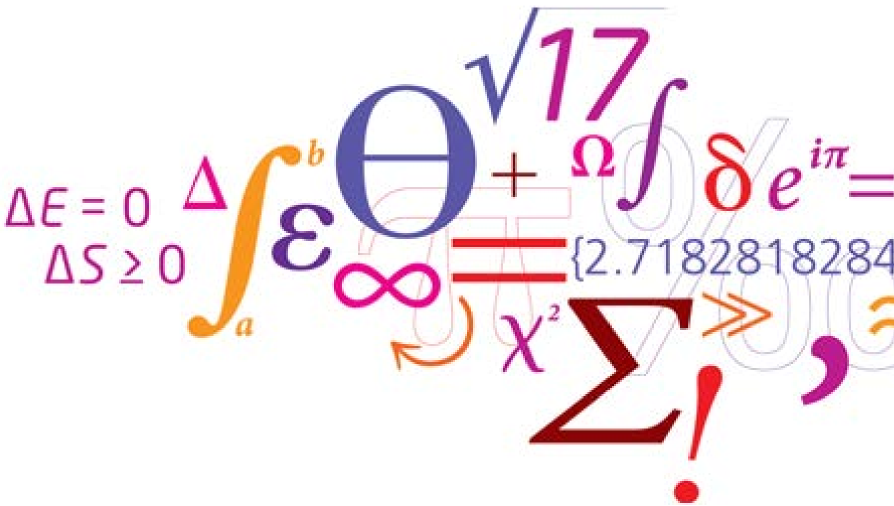
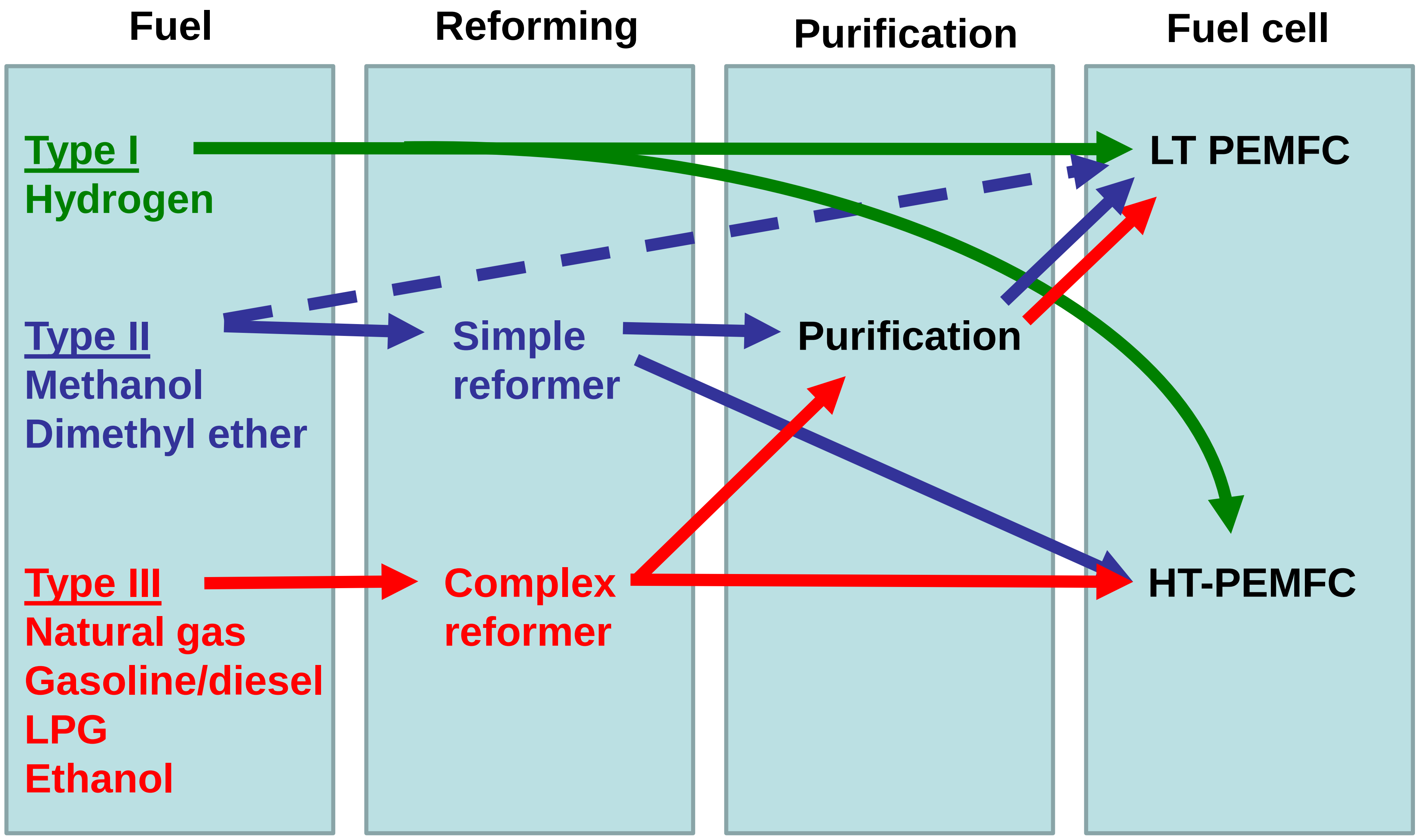


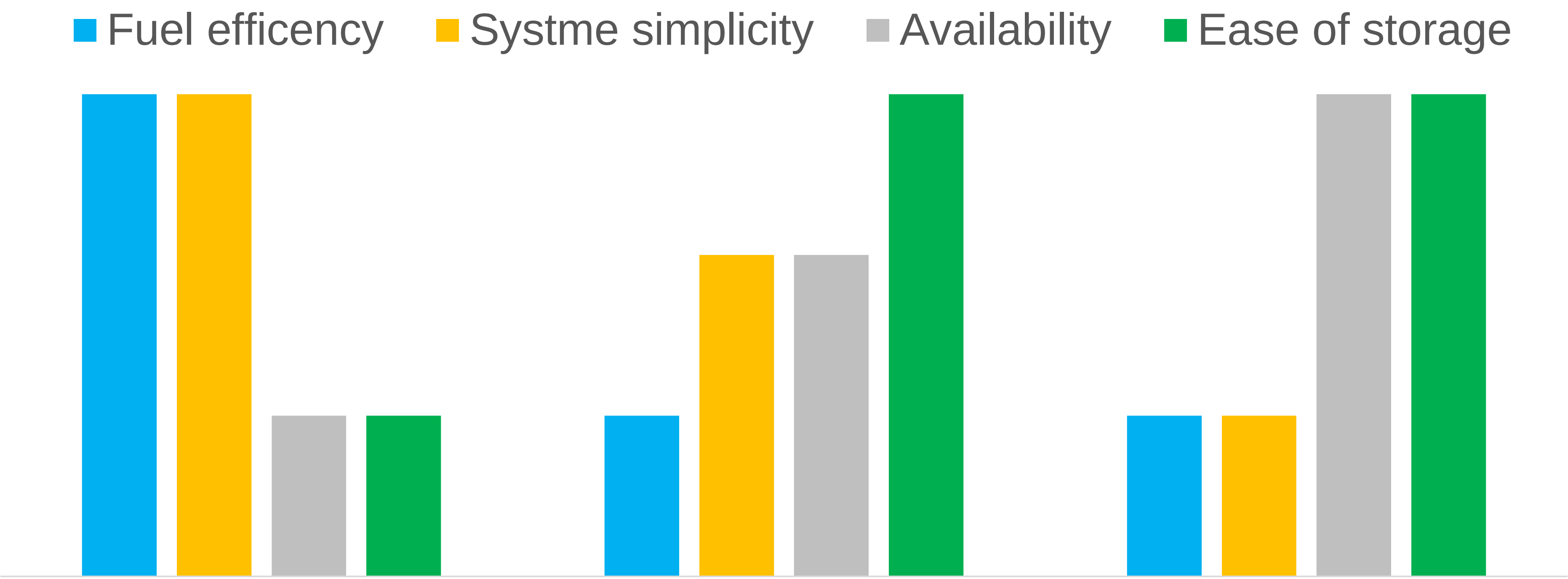
Outline

- The choice of fuel
- CO effect on the PEM fuel cell
- Binderless electrodes
- Lowering the platinum loading

Fueling of fuel cells



Fueling of fuel cells

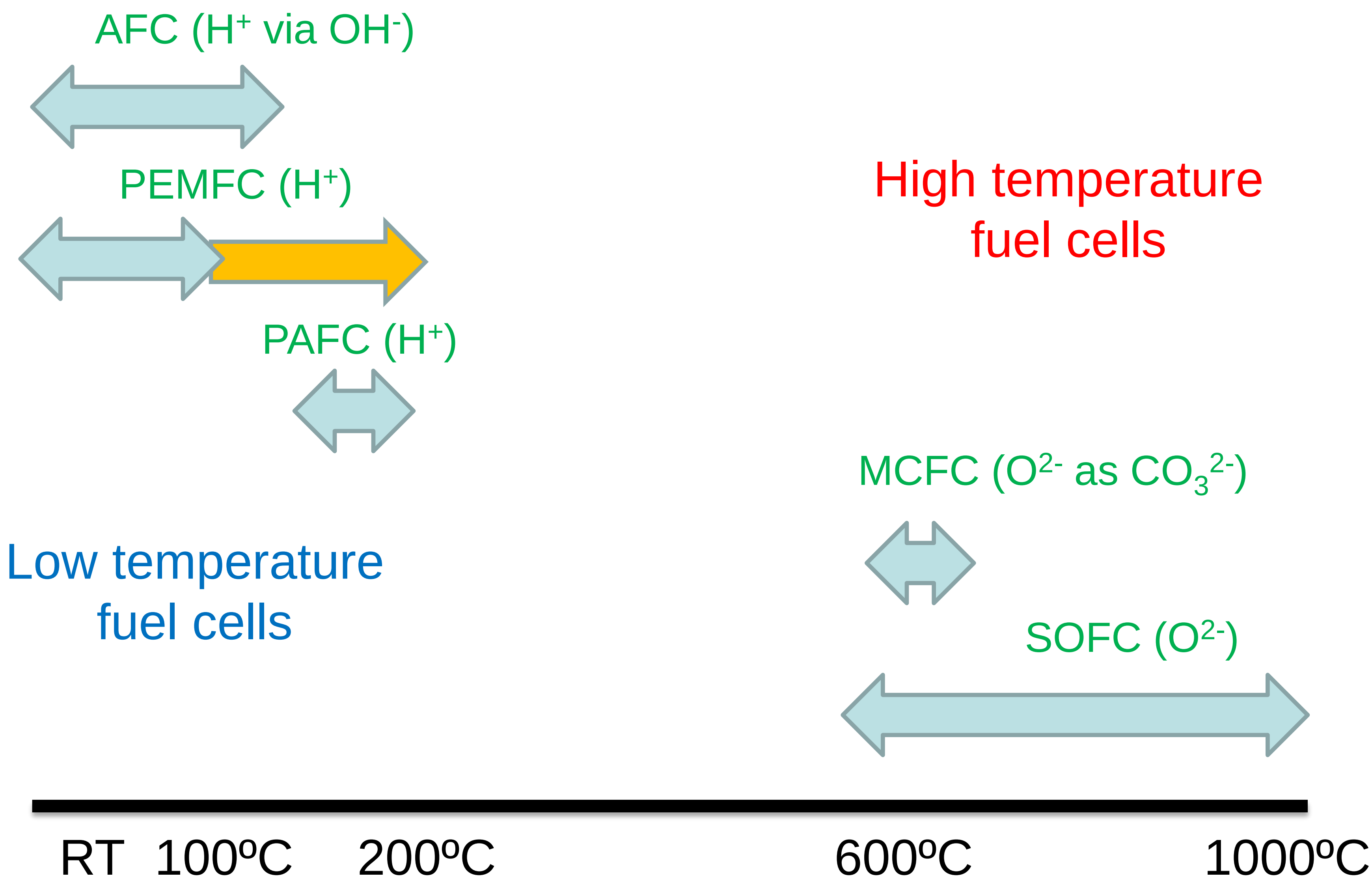


Type I
Hydrogen

Type II
Methanol
Dimethyl ether

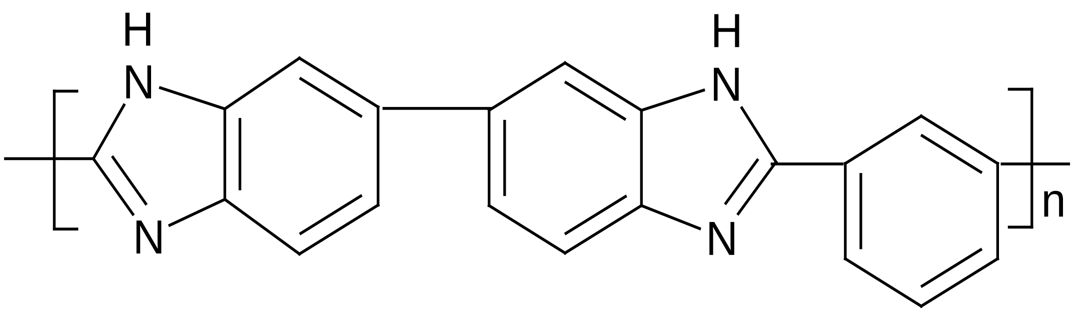
Type III
Natural gas
Gasoline/diesel
LPG
Ethanol

FC temperatures

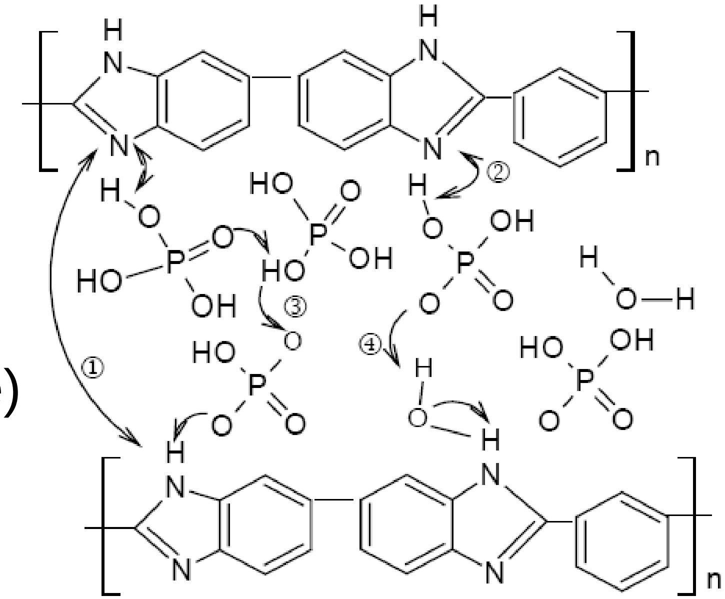


Results with PBI membranes

Polybenzimidazole



Poly (2,2´-*m*-(phenylene)-5,5´-bibenzimidazole)



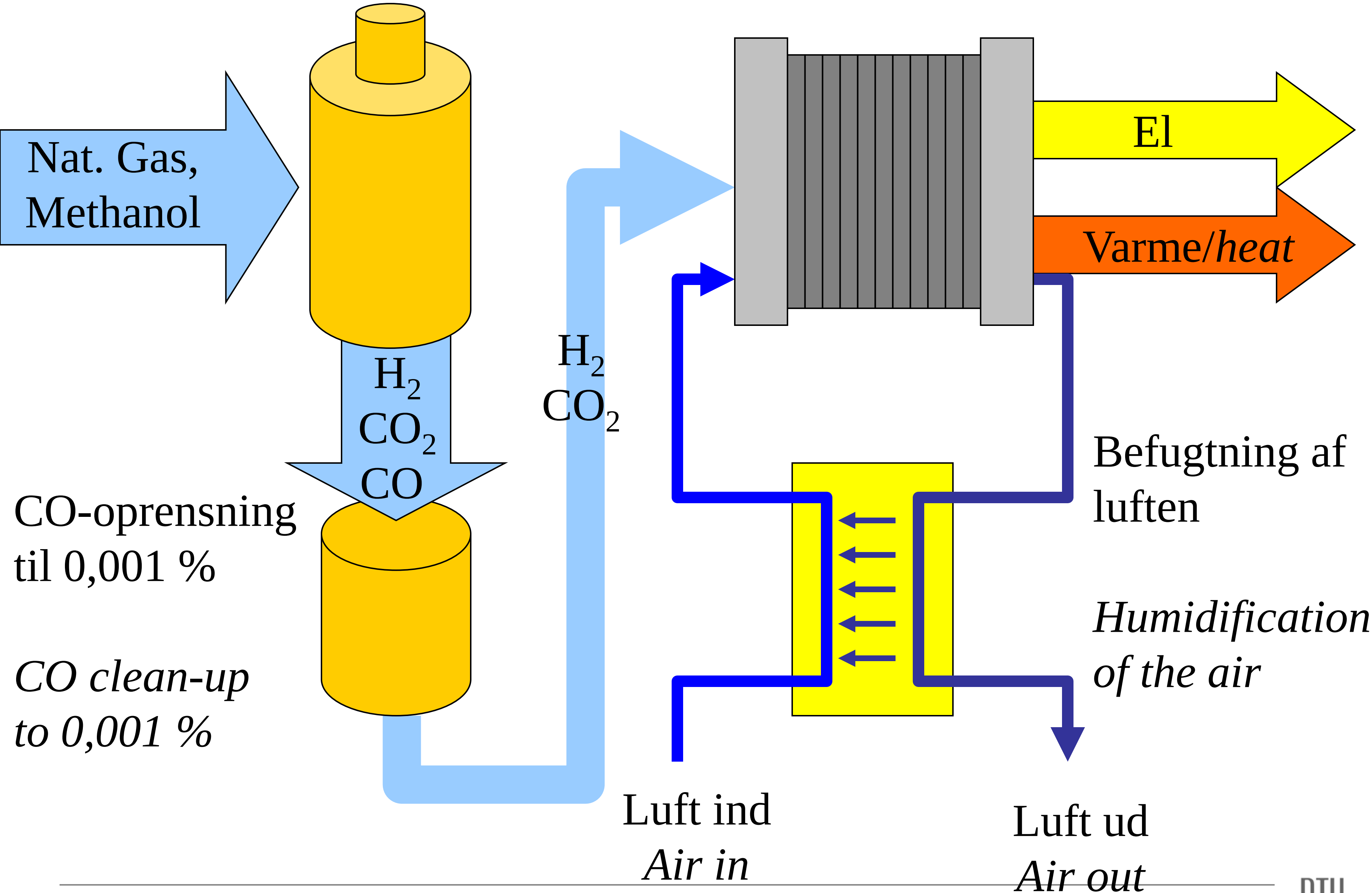
Well-known temperature resistant polymer
T_g = ~430ºC

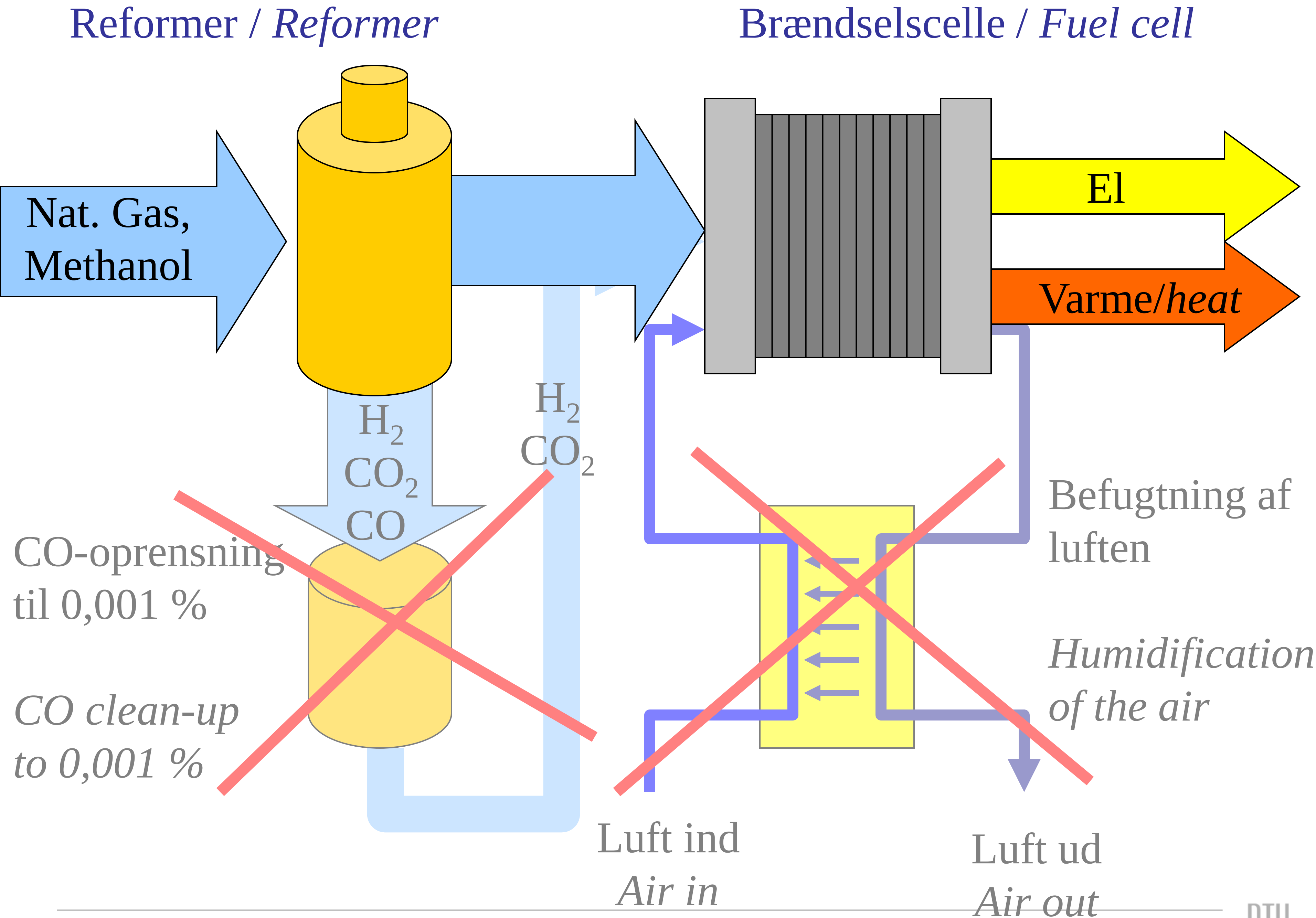
When doped with phosphoric acid:
Proton conductor

Wainright and Savinell. J. Electrochem. Soc. 142 (1995) L121

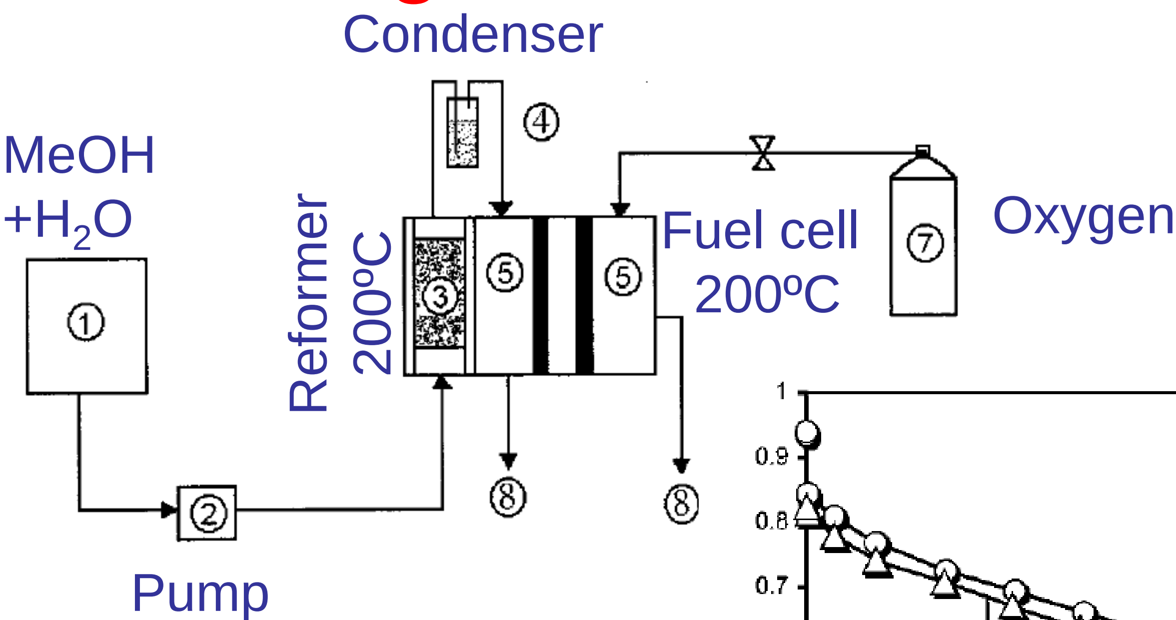
Reformer / *Reformer*

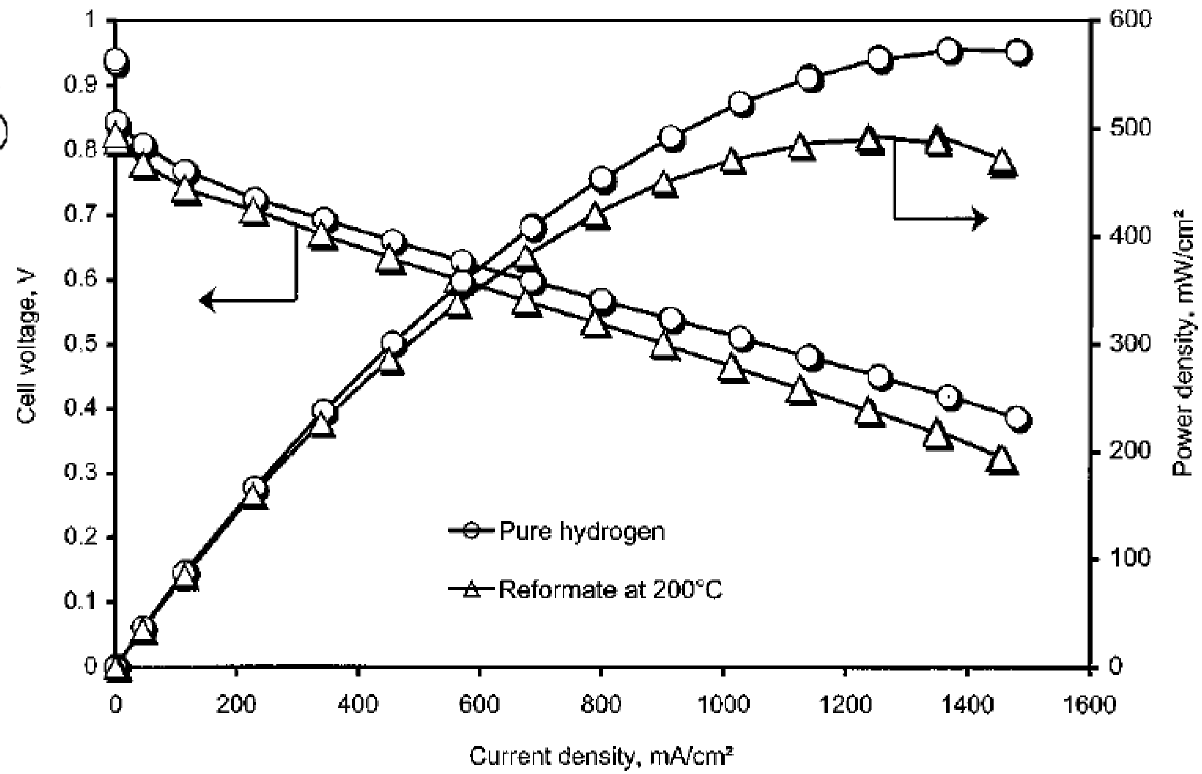
Brændselscelle / *Fuel cell*




Reformer / *Reformer*
Brændselscelle / *Fuel cell*
Nat. Gas,
Methanol
El
Varme/*heat*
H_2
CO_2
CO
H_2
CO_2
CO-oprensning
til 0,001 %
CO clean-up
to 0,001 %
Befugtning af
luften
Humidification
of the air
Luft ind
Air in
Luft ud
Air out

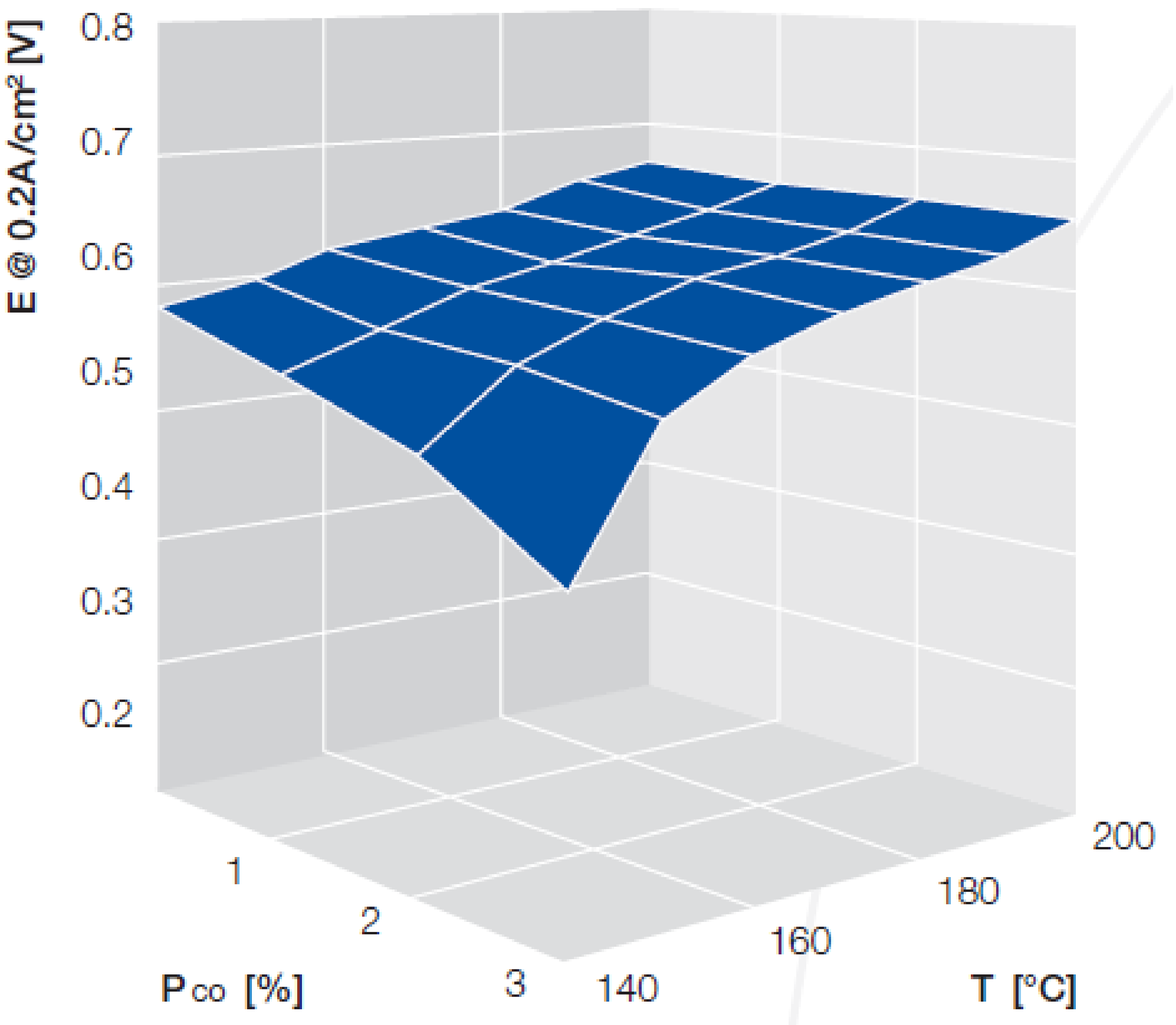
Integration with methanol reformer





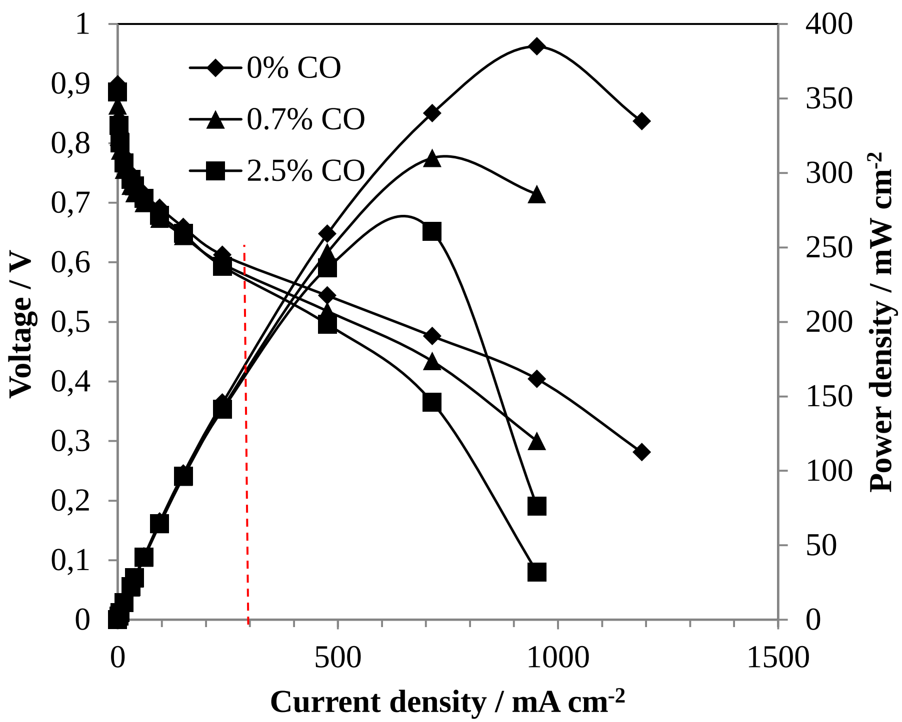
Li Qingfeng et al.
Electrochemical and Solid-State Letters, **5** (6) A125-A128 (2002)

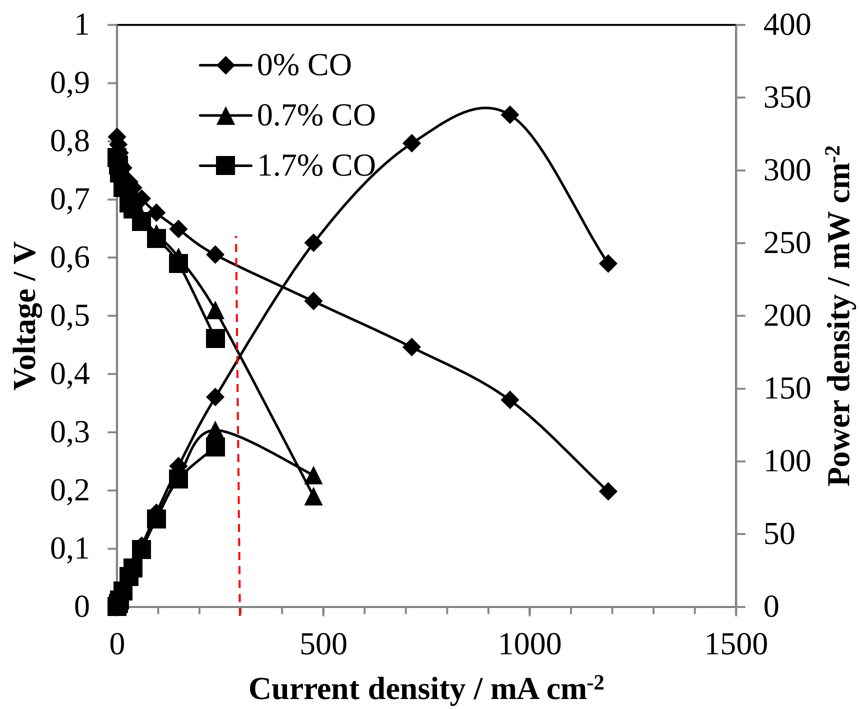
CO tolerance



BASF, Celtec® P1100W prospect

Response to diluted hydrogen





Model composition:

CO: 0.7%; H_2: 34.8%; N_2: 64.5%

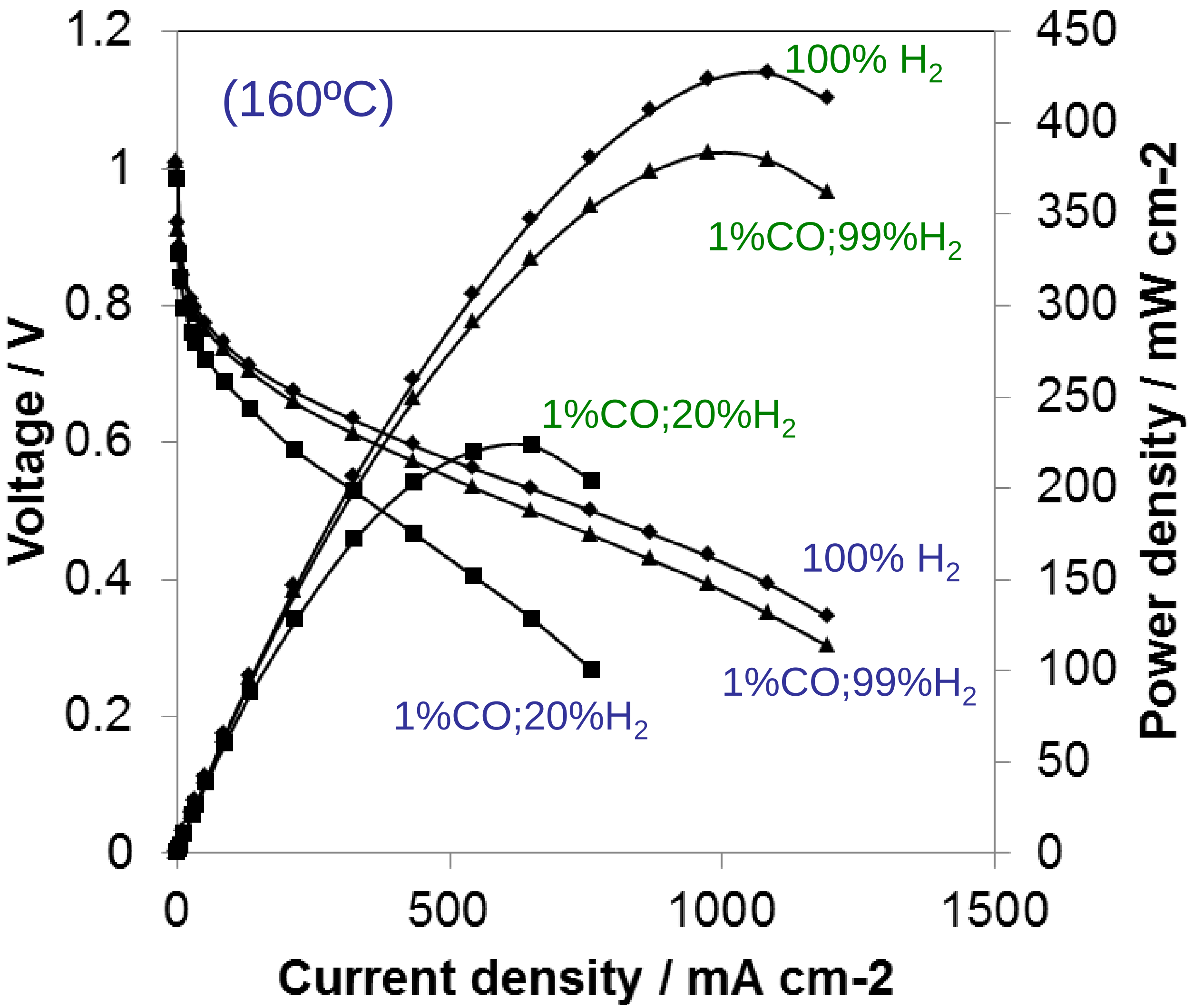
CO: 1.7%; H_2: 33.9%; N_2: 64.4%

λ_{H2} = 1.2 (0.35 mg_{Pt} cm^{-2})

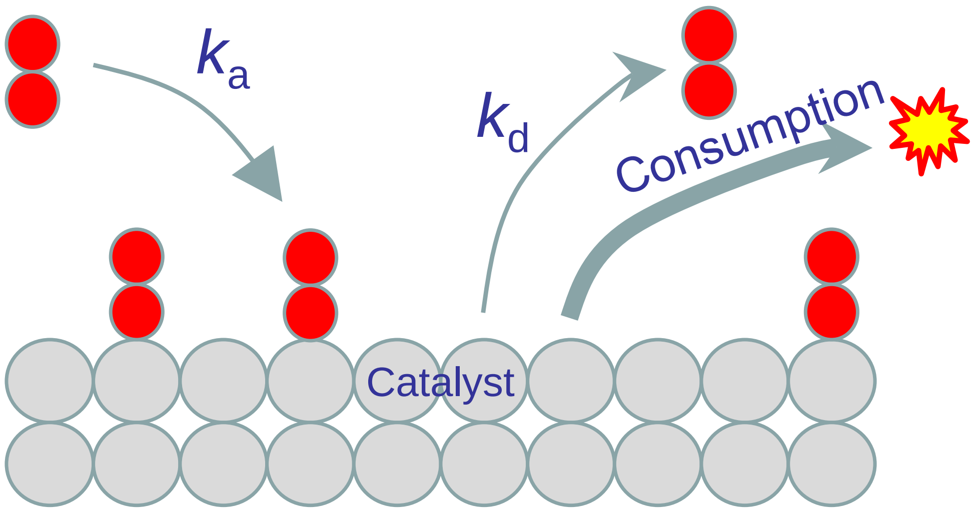
λ_{air} = 2.0 (0.83 mg_{Pt} cm^{-2})

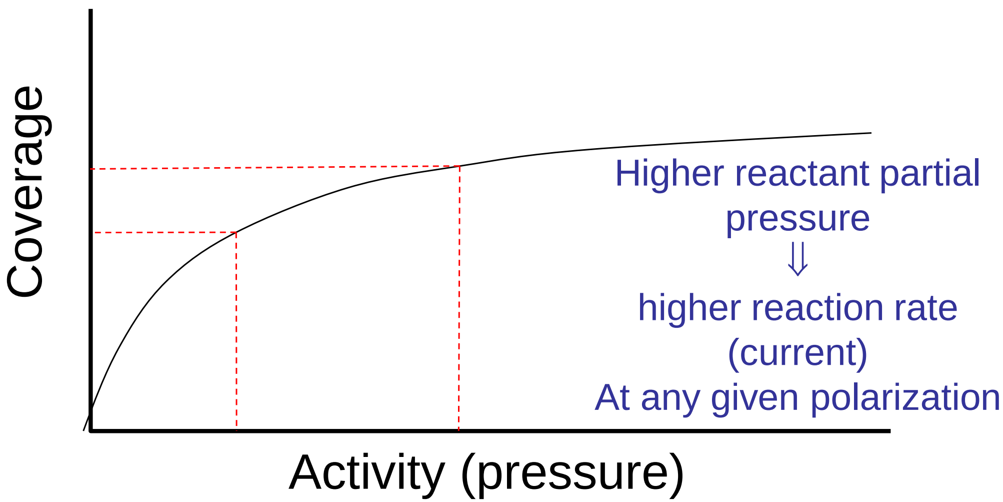
Dilution of hydrogen with CO

λ(air): 2, $\lambda(H_2)$: 1.5
Cathode: 1.3 mg_{Pt} cm^{-2}
Anode: 1.3 mg_{Pt} cm^{-2}.



High surface adsorption, Langmuir





Equilibrium:

$$k_a P N(1-\theta) = k_d N\theta$$

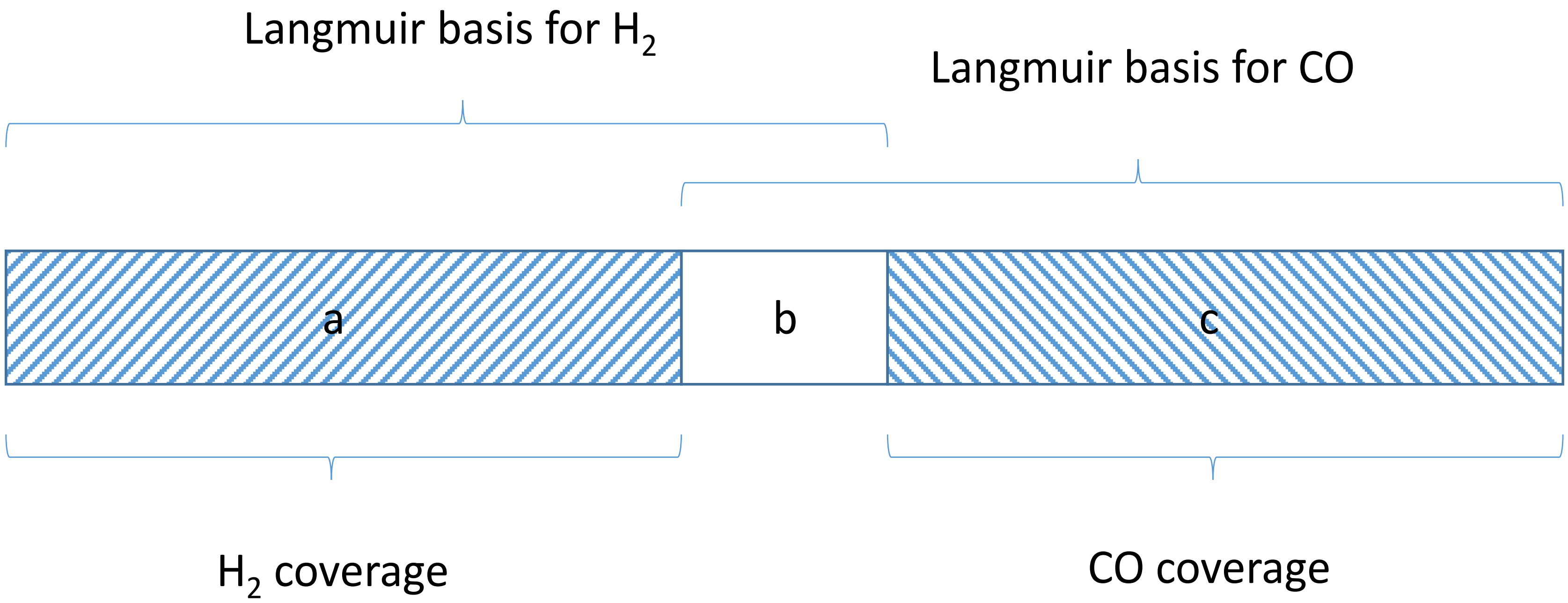
or:

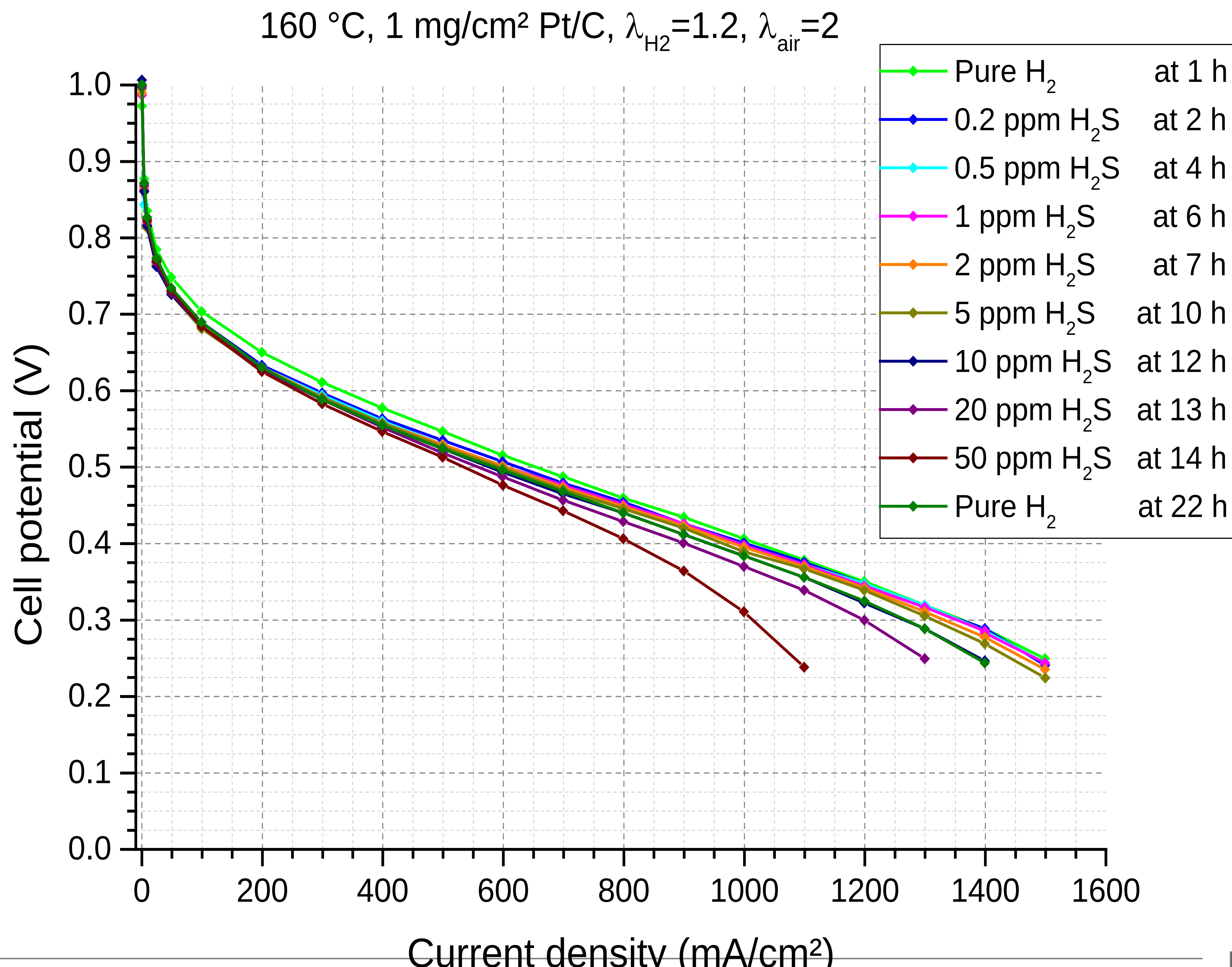
$$\theta = \frac{\frac{k_a}{k_d}P}{1+\frac{k_a}{k_d}P} = \frac{KP}{1+KP}$$

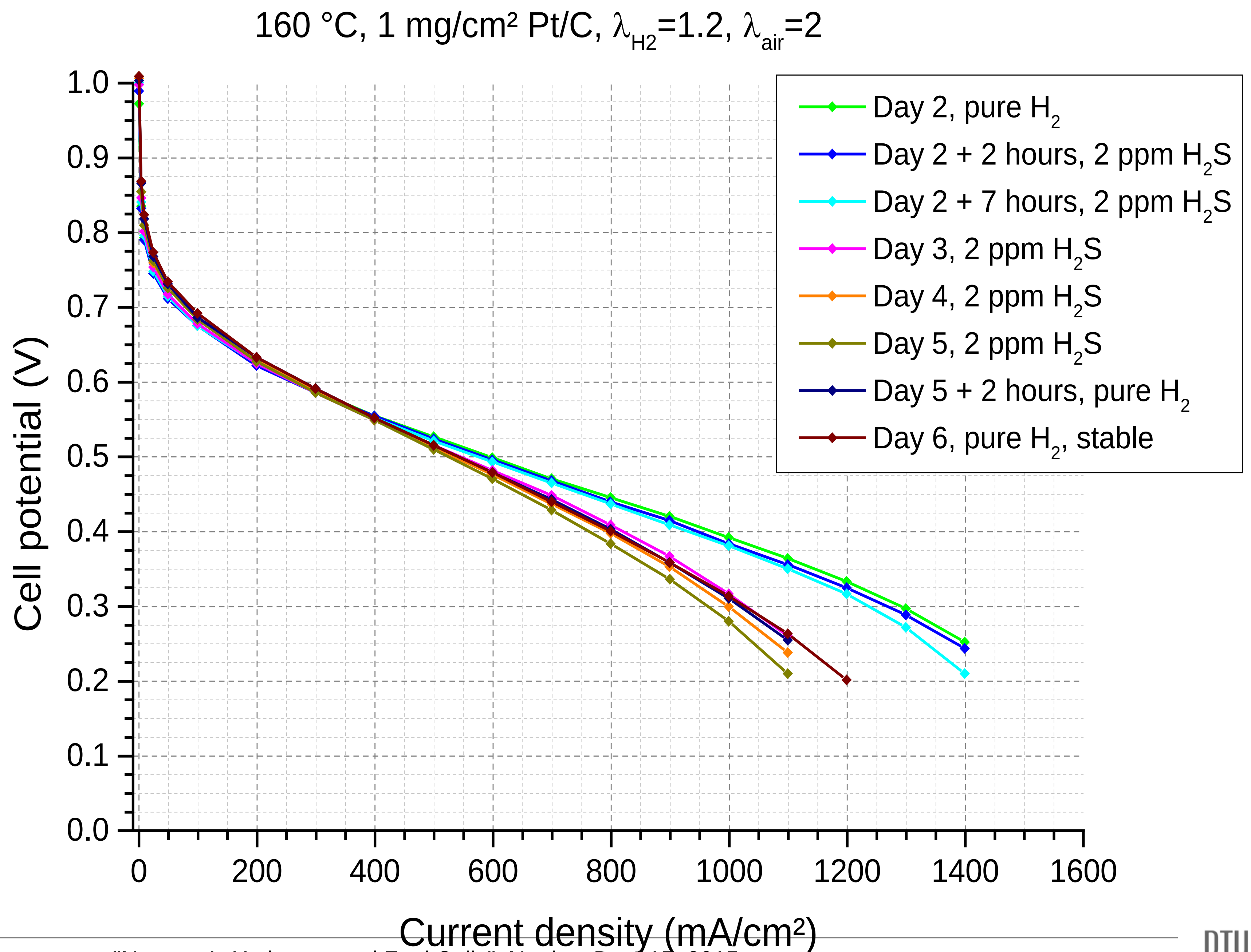
N: no. of sites
θ: surface fraction occupied
P: pressure
t: time
k_a, k_d: rate constants for adsorption and desorption

$K = K(T)$

Competition with CO




160 °C, 1 mg/cm² Pt/C, λH2=1.2, λair=2
Pure H2 at 1 h
0.2 ppm H2S at 2 h
0.5 ppm H2S at 4 h
1 ppm H2S at 6 h
2 ppm H2S at 7 h
5 ppm H2S at 10 h
10 ppm H2S at 12 h
20 ppm H2S at 13 h
50 ppm H2S at 14 h
Pure H2 at 22 h
Cell potential (V)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
1200
1400
1600
Current density (mA/cm²)



160 °C, 1 mg/cm² Pt/C, λH2=1.2, λair=2
Cell potential (V)
Current density (mA/cm²)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0
200
400
600
800
1000
1200
1400
1600
Day 2, pure H2
Day 2 + 2 hours, 2 ppm H2S
Day 2 + 7 hours, 2 ppm H2S
Day 3, 2 ppm H2S
Day 4, 2 ppm H2S
Day 5, 2 ppm H2S
Day 5 + 2 hours, pure H2
Day 6, pure H2, stable

Reduction of binder

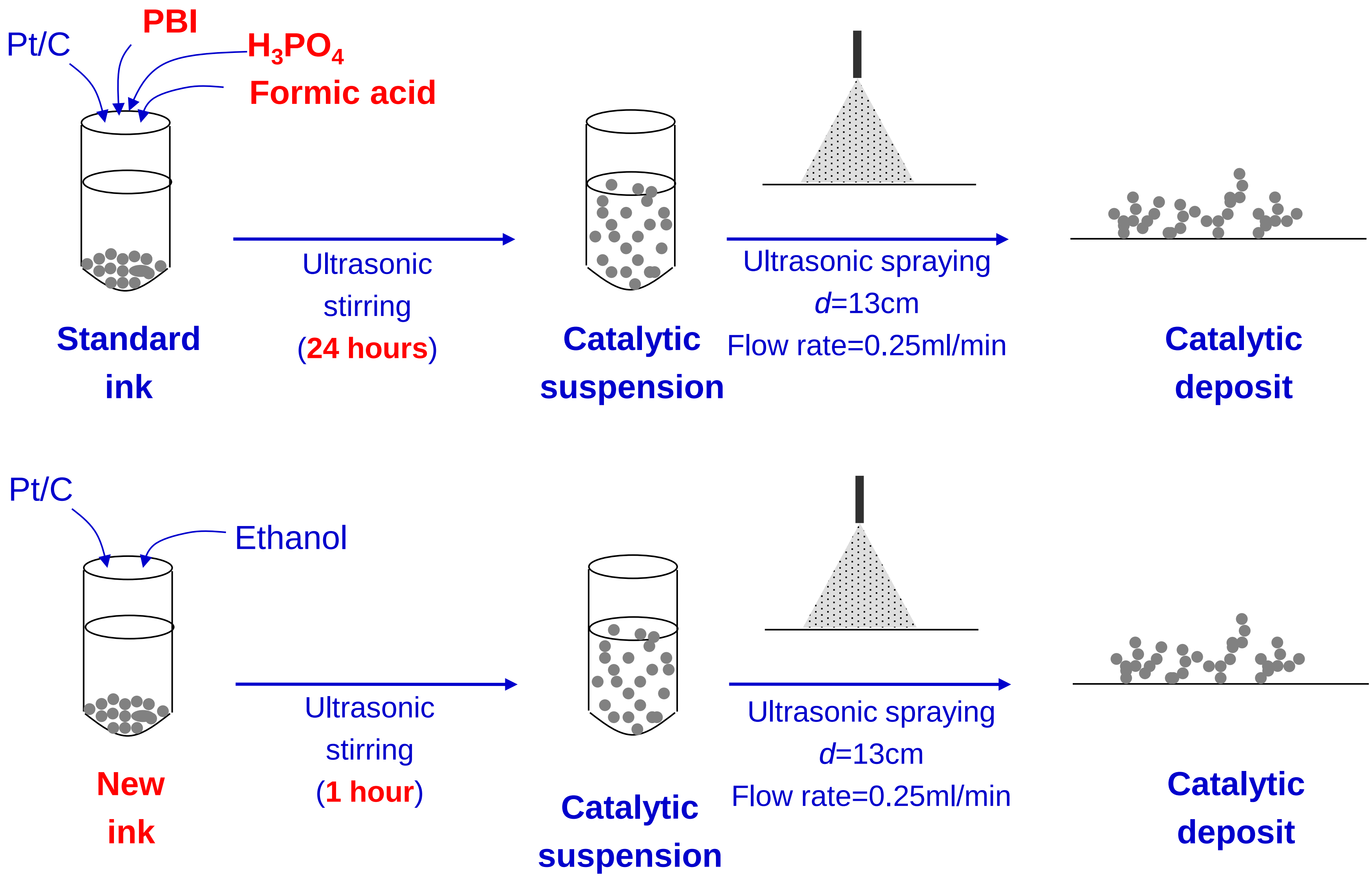
Experiments say:
Less binder (PBI) gives better performance.

What is the optimum/minimum?

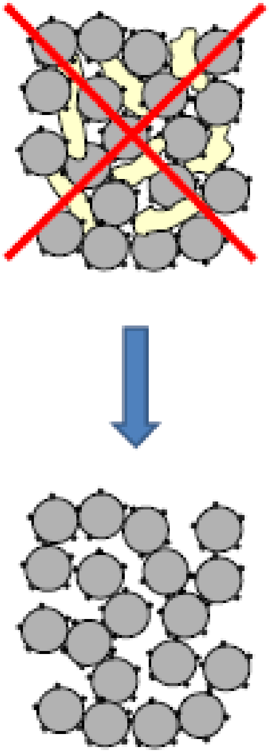
What happens if we go to the extreme and make electrode completely without the binder?

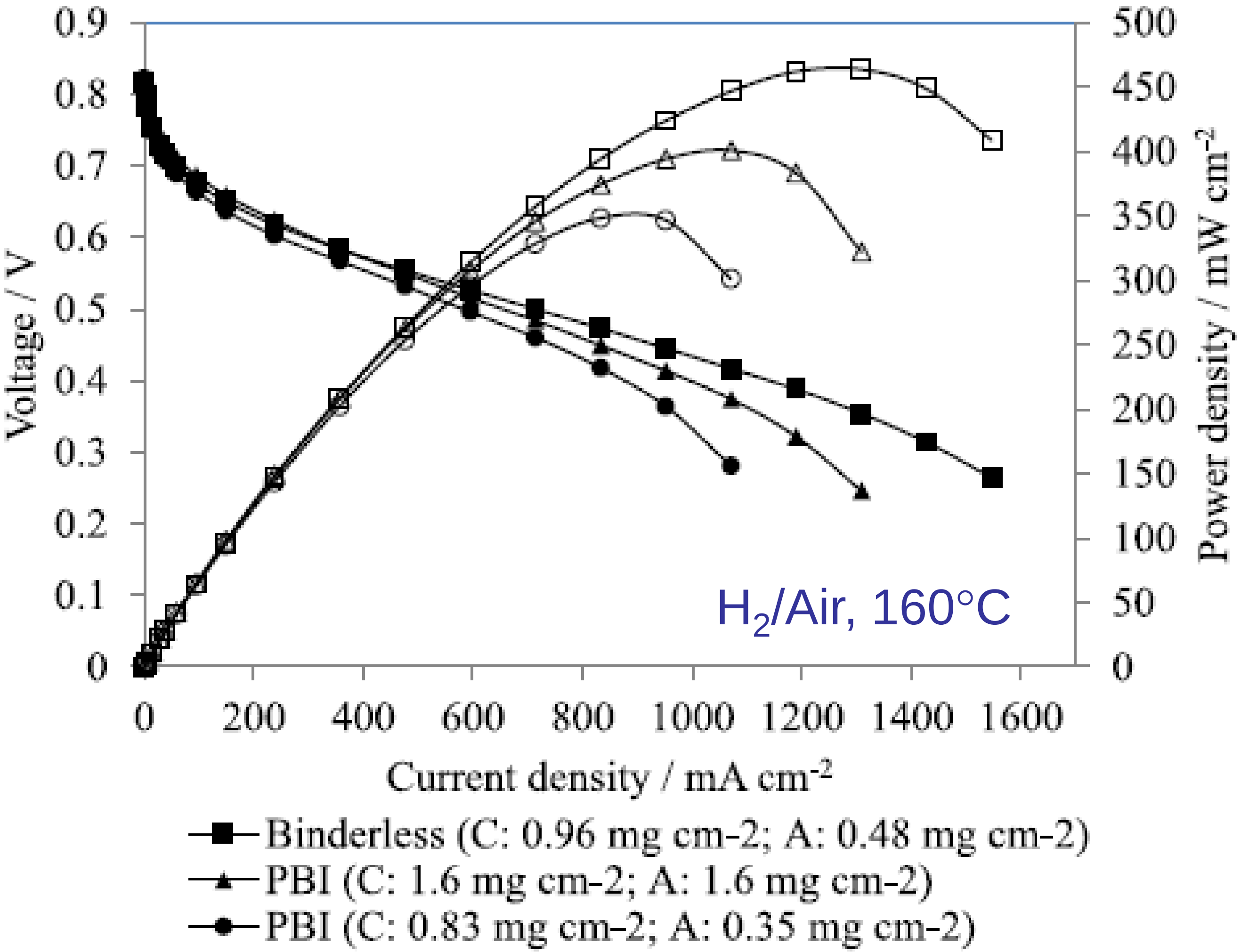
1. Nothing. The binder is not needed
2. The catalyst layer falls off too easily
3. The proton transport is mostly blocked
4. Reduction to a certain level improved performance and then it breaks down

Single cell dev., binderless electrodes



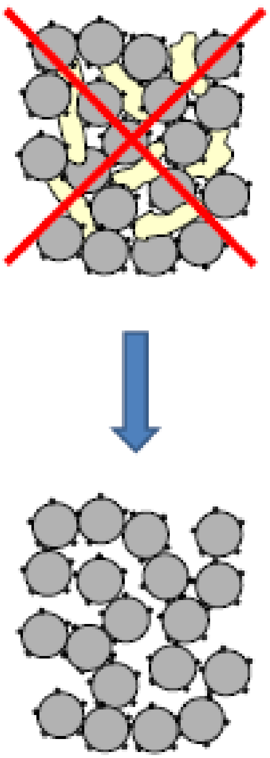
Binderless electrodes

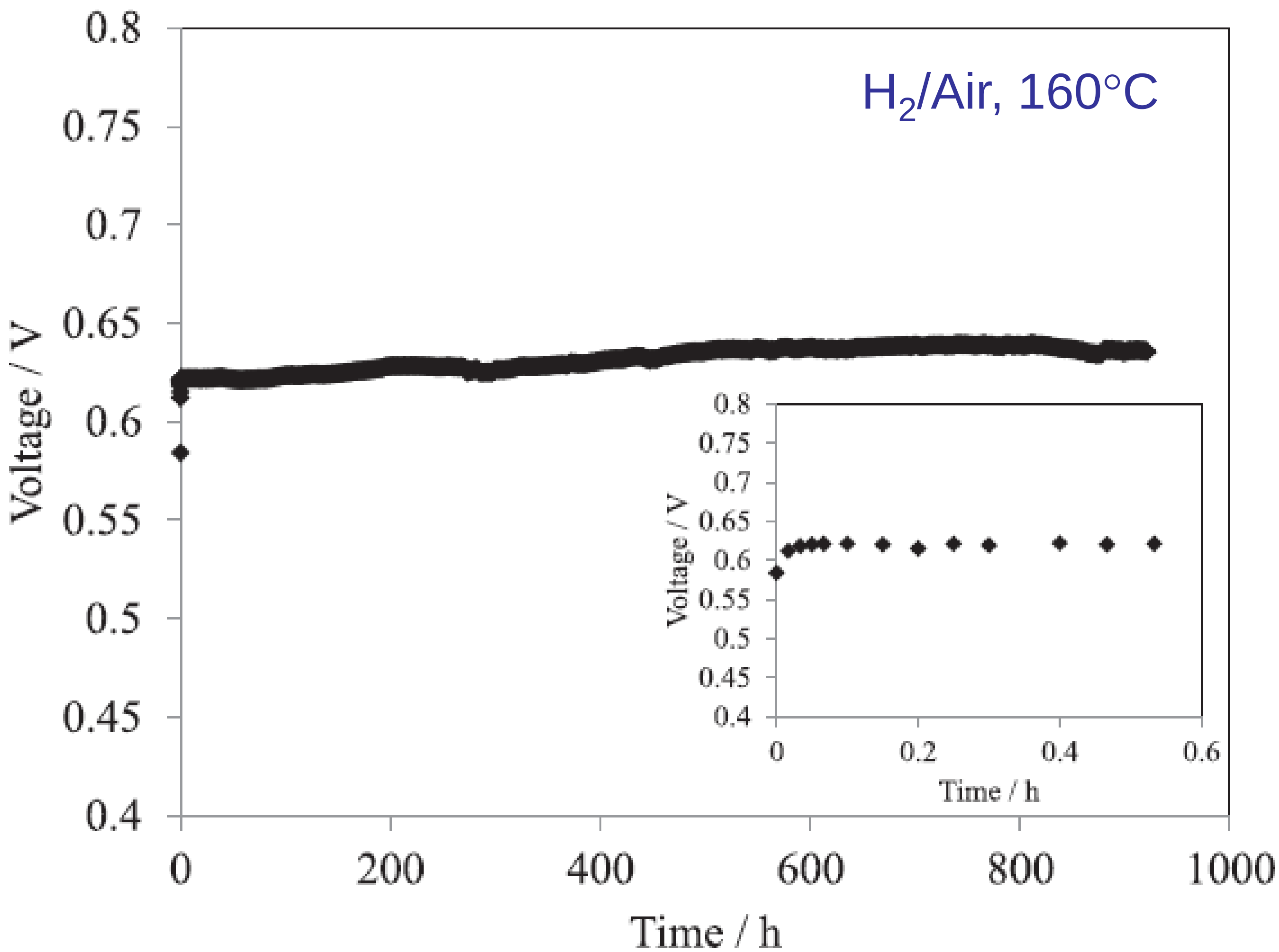




S. Martin, Q. Li, T. Steenberg, J.O. Jensen.
J. Power Sources 272 (2014) 559-566

Binderless electrodes





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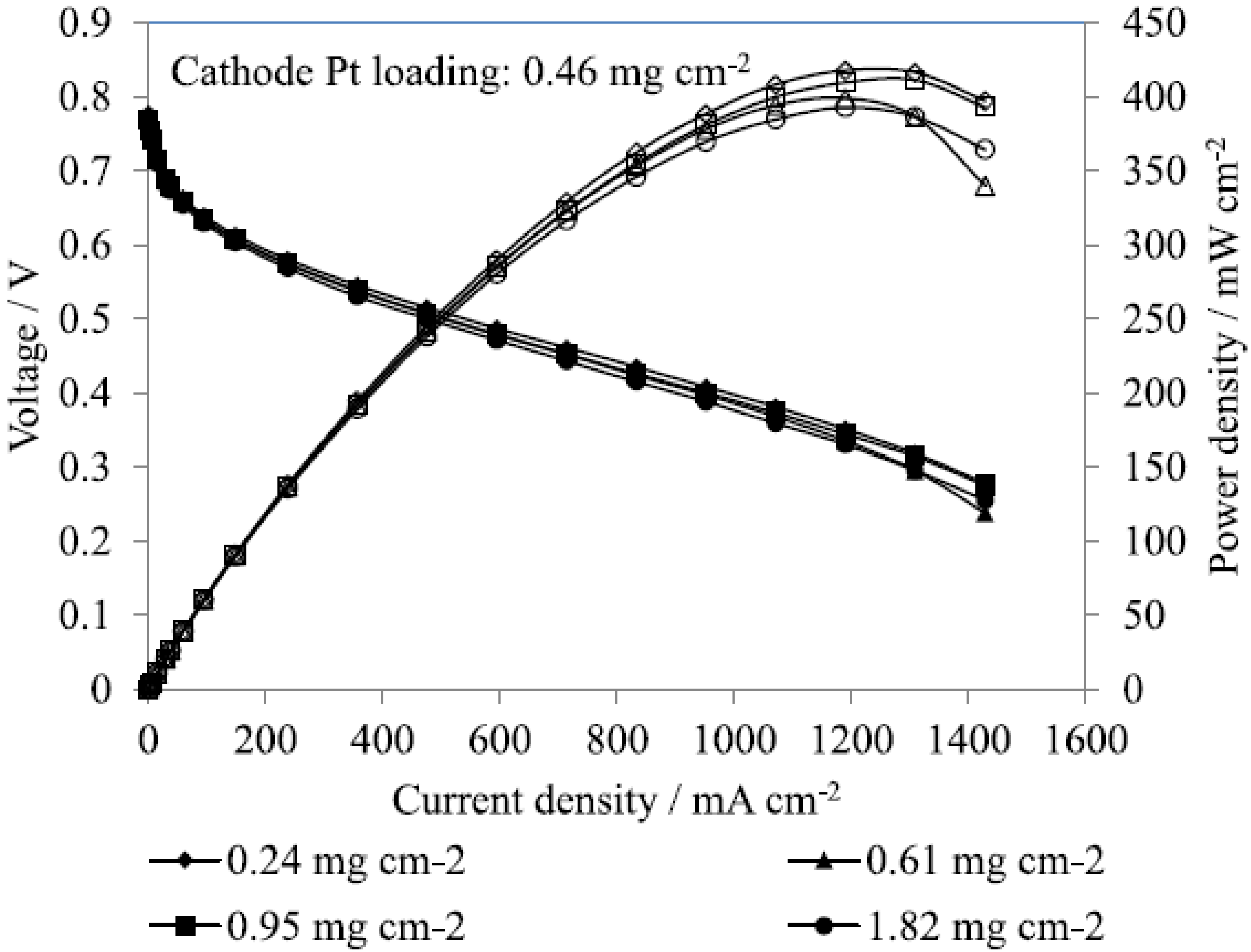
Reducing Pt loading on anode



S. Martin, Q. Li, T. Steenberg, J.O. Jensen.
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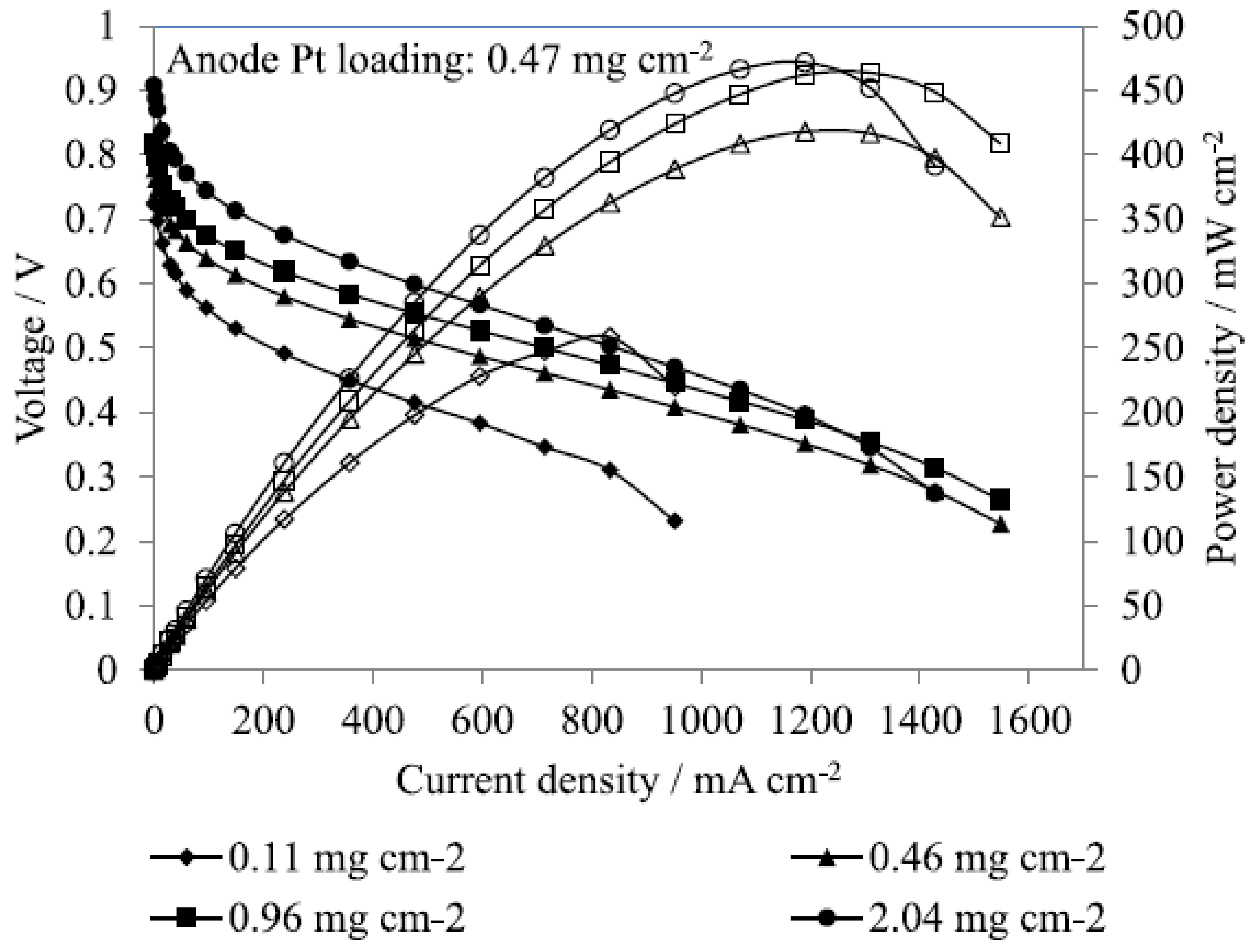
Reducing Pt loading on cathode



S. Martin, Q. Li, T. Steenberg, J.O. Jensen.
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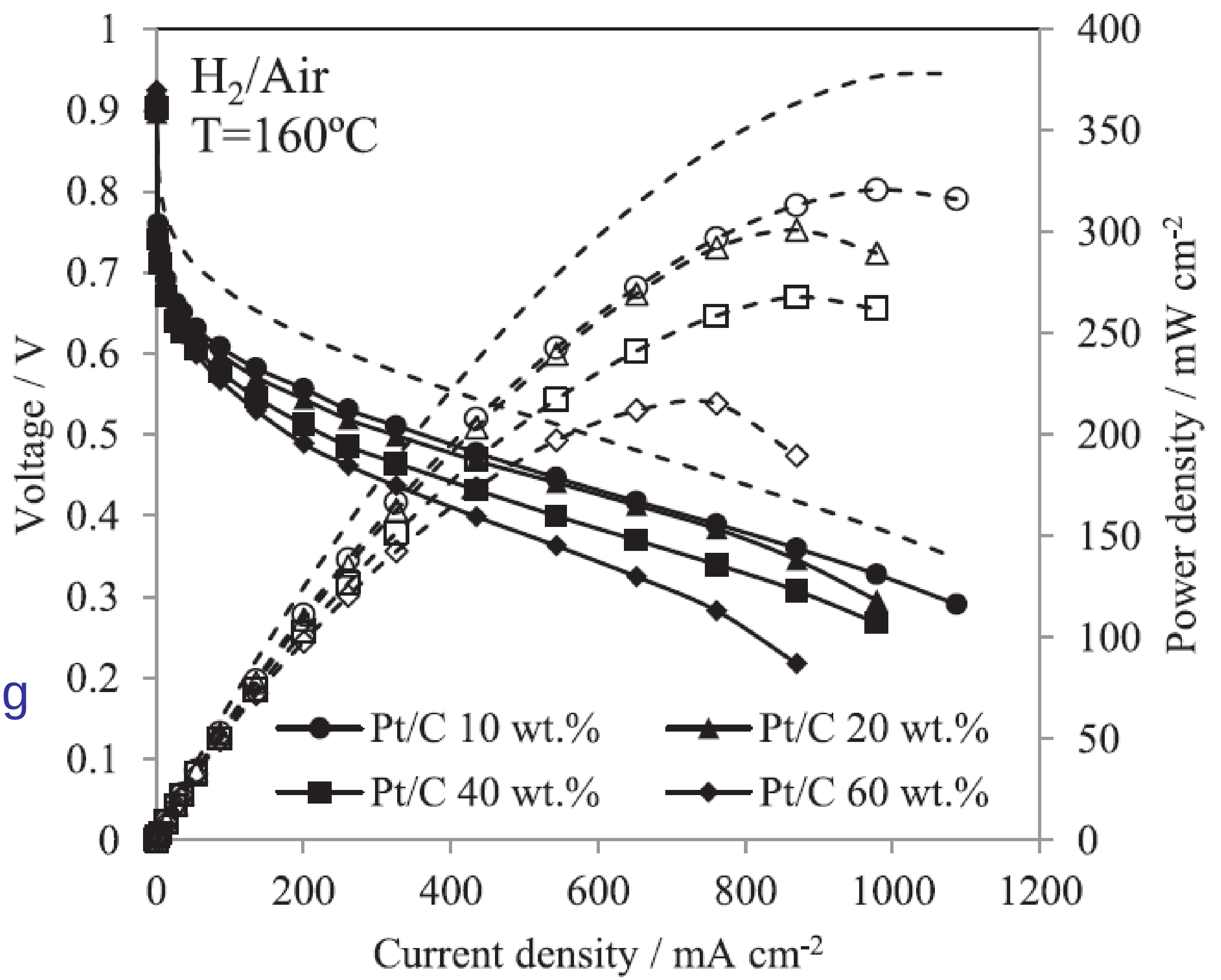
Reducing Pt loading to 0.1 mg_{Pt} /cm^2 (each)

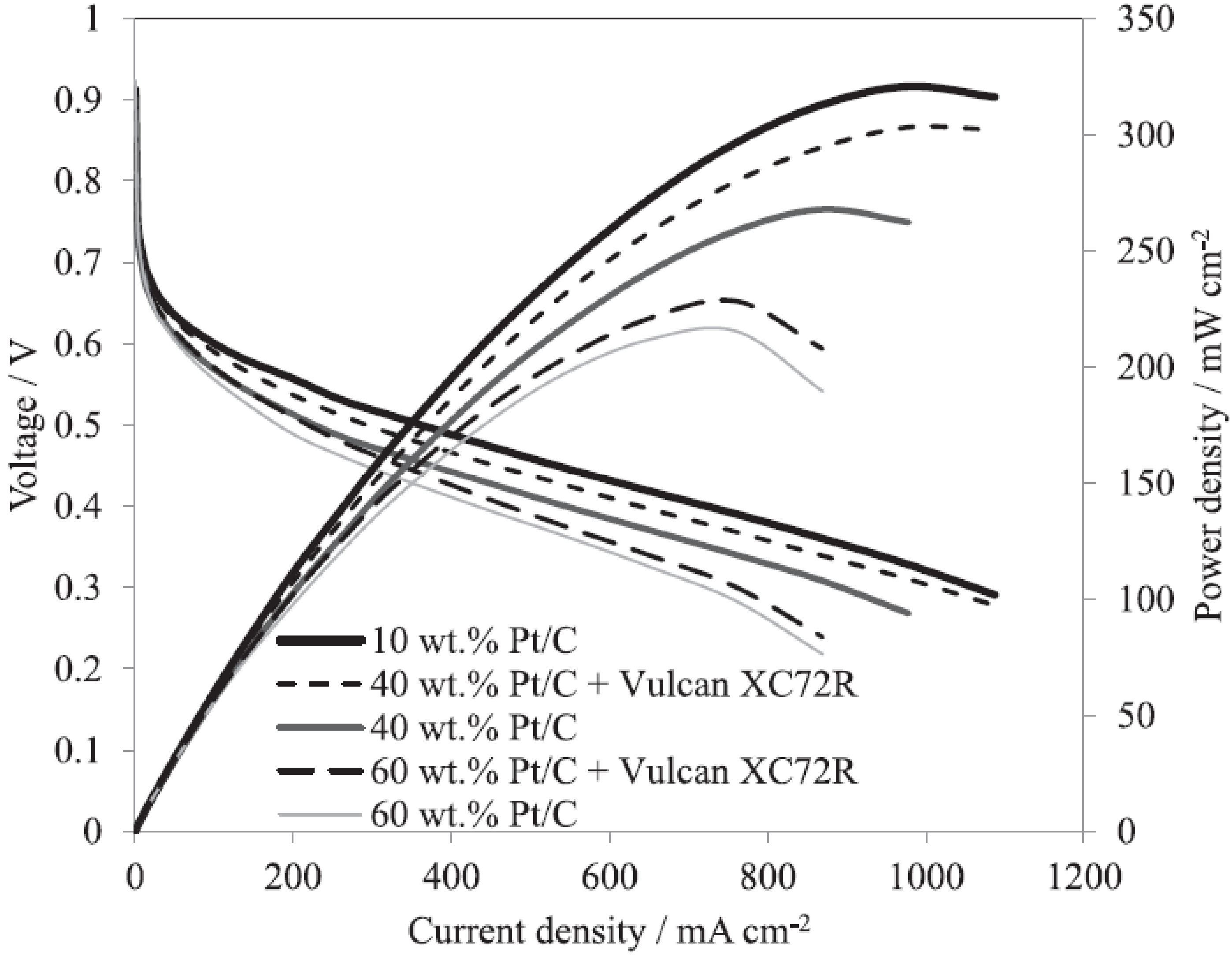


No markers:
SOA, 0.6/0.6 mg

Markers:
0.1/0.1 mg

S. Martin, Q. Li, J.O. Jensen.
J. Power Sources 293 (2015) 51-56

Reducing Pt loading to 0.1 mg_{Pt} /cm^2



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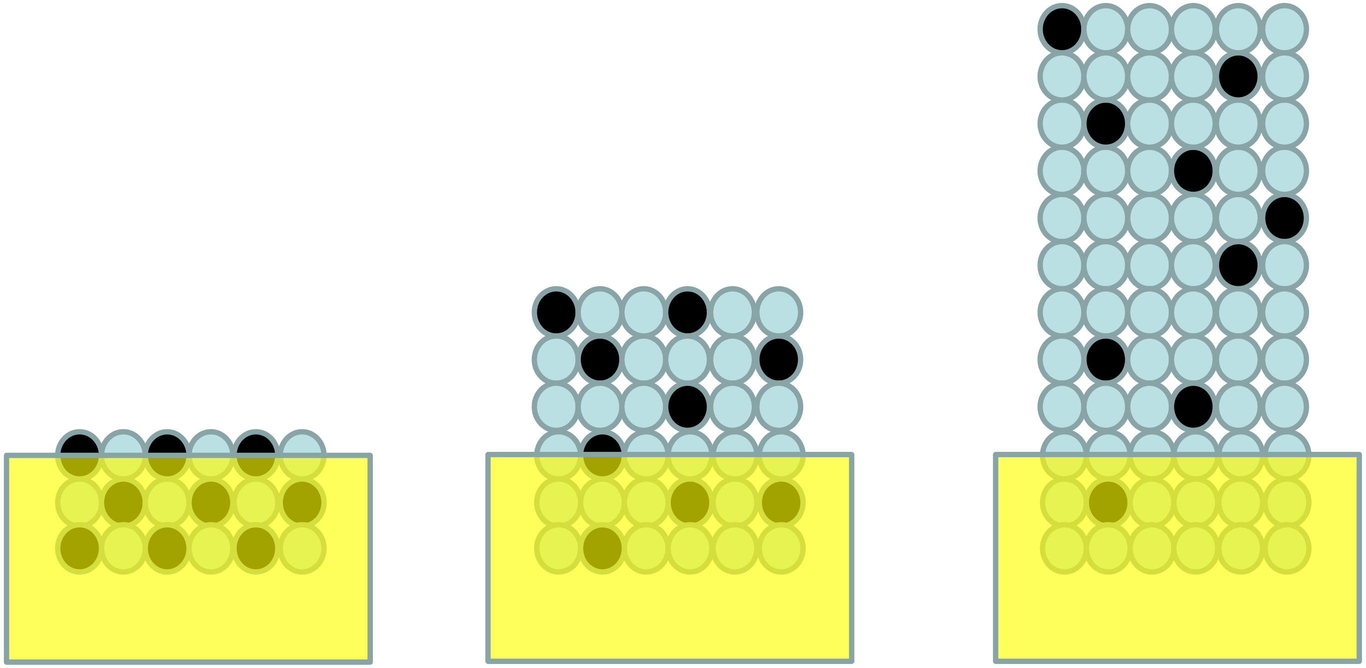
J. Power Sources 293 (2015) 51-56

A closer look a the catalyst materials (JM)

Pt on carbon / wt.%	10	20	40	60
Pt loading cathode/anode / mg cm^{-2}	0.098/0.094	0.098/0.094	0.098/0.096	0.098/0.098
Peak power density[a] / mW cm^{-2}	321(482)	301	268	215
Pt utilization[a] / kWg_{Pt}^{-1} overall cathodic	 1.67(2.51) 3.27(4.92)	 1.57 3.08	 1.38 2.73	 1.10 2.19
Voltage at 200 mA $cm^{-2,a}$ / V	0.557(0.618)	0.544	0.513	0.489
Catalyst layer thickness / µm	~ 18	~ 8	~ 3.5	~ 2.5
Pt XRD crystallite size[b] / nm	2.5	2.7	3.3	3.2

Partial flooding?



Acknowledgement

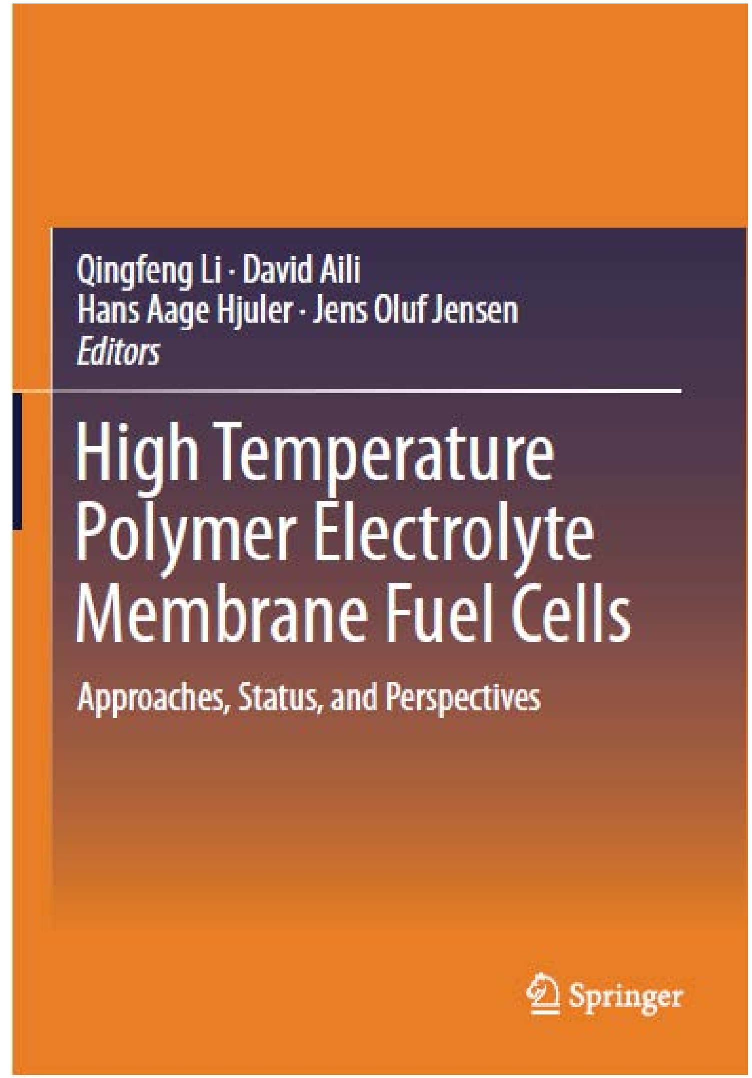
pure

" Development of Auxiliary Power Unit for Recreational yachts " (PURE)

Grant agreement no: 303457

Seventh Framework Programme

FCH
FUEL CELLS AND HYDROGEN JOINT UNDERTAKING



Book, Springer 2015